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| 3 | Vadose Zone Remediation of CO ₂ Leakage from |
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| 5 | Geologic CO ₂ Storage Sites |
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Abstract

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In the unlikely event that carbon dioxide (CO₂) leakage from deep geologic CO₂ storage sites reaches the vadose zone, remediation measures for removing the CO₂ gas plume may have to be undertaken. Carbon dioxide leakage plumes are similar in many ways to volatile organic compound (VOC) vapor plumes, and the same remediation approaches are applicable. We present here numerical simulation results of passive and active remediation strategies for CO₂ leakage plumes in the vadose zone. The starting time for the remediation scenarios is assumed to be after a steady-state CO₂ leakage plume is established in the vadose zone, and the source of this plume has been cut off. consider first passive remediation, both with and without barometric pumping. Next, we consider active methods involving extraction wells in both vertical and horizontal configurations. In order to compare the effectiveness of the various remediation strategies, we define a half-life of the CO₂ plume as a convenient measure of the CO₂ removal rate. For CO₂ removal by passive remediation approaches such as barometric pumping, thicker vadose zones generally require longer remediation times. However, for the case of a thin vadose zone where a significant fraction of the CO₂ plume mass resides within the high-liquid saturation region near the water table, the half-life of the CO₂ plume without barometric pumping is longer than for somewhat thicker vadose zones. As for active strategies, results show that a combination of horizontal and vertical wells is the most effective among the strategies investigated.

Introduction

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Geologic carbon sequestration is the direct injection of carbon dioxide (CO₂) deep into geological formations for long-term storage for the purpose of reducing the rate of increase of atmospheric CO₂ concentrations due to energy production from fossil fuels. Although there are many mechanisms to trap the injected CO₂ (Bachu et al., 1994; Oldenburg and Unger, 2003), there is the risk that injected CO₂ will migrate away from the primary target formation (Holloway, 1997), a process referred to as leakage by Oldenburg and Unger (2003). Possible leakage pathways include wells (abandoned or active), permeable faults and fractures, and unexpected fast-flow paths. Figure 1 is a conceptual diagram showing a variety of possible leakage pathways and processes. Leakage will likely lead to secondary trapping in shallower formations, or result in a flow path with a sufficiently long travel time so as to meet the sequestration objective. However, there is a risk that CO₂ leakage will lead to rapid migration upward to the vadose zone. Seepage happens when leaked CO₂ migrates through the vadose zone, reaches the ground surface, and escapes into the ambient air (Oldenburg and Unger, 2003). Seepage of CO₂ can lead to locally high CO₂ concentrations in the near-surface environment, which may cause health and environmental hazards. Although CO₂ leakage to the vadose zone is highly unlikely, it is useful to demonstrate that effective remediation strategies exist for CO₂ leakage plumes in the vadose zone should such measures ever be necessary. In the context of Figure 1, this study focuses on the uppermost part of the subsurface where a CO₂ leakage plume exists within the vadose zone.

The objective of this work is to explore the effectiveness of various remediation 2 strategies for CO₂ leakage plumes in the vadose zone. The approach we take is numerical 3 4 5 6 7

accomplished effectively by standard approaches.

simulation of both passive and active remediation strategies that involve CO₂ removal from the vadose zone. Such strategies have been developed and implemented over the last 25 years for the removal of contaminant vapors such as those from volatile organic compounds (VOCs) that have leaked into the vadose zone from surface leaks and spills, and from underground storage tanks. In this study, we compare removal rates of CO₂ plumes from the vadose zone under passive and active treatment processes. In so doing, we demonstrate that remediation of CO2 leakage plumes in the vadose zone can be

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Background

The migration of CO₂ through the vadose zone has some similarity to the transport of VOCs in the vadose zone. In particular, CO2 is a dense gas relative to air. Similarly, the high molecular weights and high vapor pressures of common contaminant VOCs give rise to dense VOC gas plumes emanating from non-aqueous phase liquid (NAPL) VOC leaks and spills (Falta et al., 1989). At a temperature of 25 °C and a pressure of 1 atm., the density of air is 1.17 kg m⁻³, while the density of VOCs ranges from 1.21 kg m⁻³ (Xylene) to 2.50 kg m⁻³ (Methylene chloride) (Falta et al., 1989), and CO₂ has a density of 1.81 kg m⁻³. Falta et al. (1989) studied under what conditions the density-driven gas flow may dominate the transport of contaminants in the gas phase. The conclusion was that the magnitude of density-driven effects on transport depends on both the chemical's saturated vapor density, and the degree to which the chemical is partitioned from the gas

2 phase into the water and solid phases. The effects of density-driven gas flow are only

apparent when the permeability of the porous medium is large enough to sustain

4 significant gas flow.

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Although CO₂ and VOC vapors share some similarities in density, there are very important differences between them relevant to remediation and transport. With regard to the need for remediation, the main difference between VOCs and CO2 is that VOCs are potentially harmful to humans and other animals even at low concentrations. In contrast, CO₂ is naturally occurring, ubiquitous, and essential to life. The background atmospheric CO₂ concentration is approximately 350 ppmv, and CO₂ is relatively harmless even at concentrations many times the background concentration. However, long-term exposure to CO2 at concentrations of a few percent or higher can be harmful to humans, other animals, and the roots of plants. Another difference between CO2 leakage plumes and VOC contaminant plumes is the typical location of the source and transport direction. In general, vadose zone VOC plumes tend to flow downward through the vadose zone from above due to leaking underground tanks, and surface spills. In contrast, potential CO₂ leakage plumes will typically arrive from below. A significant physical difference between VOC vapors and CO₂ is that CO₂ has a high solubility in water, approximately 50 times that of air at 1 bar, 20 °C. VOCs on the other hand, are generally much less soluble in water, with the well known exception of methyl tertiary-butyl ether (MTBE), whose high solubility and non-biodegradability has made it one of the most costly subsurface contaminants (EPA, 1998). The high solubility and large density of CO₂ will

make CO₂ leakage plumes tend to pond on the water table or be trapped as a dissolved

2 component in the water in the vadose zone. Finally, CO₂ dissolution in water forms

3 carbonic acid which leads to the lowering of pH and the potential for corrosion of metals

in extraction systems, a feature that may require special attention in practical

5 applications.

Soil vapor extraction (SVE) is a technology developed to remove VOCs and some semivolatile organic compounds (SVOCs) from the vadose zone, a comprehensive review of which has been presented by Wilson (1995). SVE system design options usually include vertical or horizontal wells screened in the contaminated zone as well as trenches. SVE has been widely used for the remediation of spills, leaks, and hazardous waste sites during the past 25 years due to its efficiency and relatively low cost. A significant number of modeling efforts including analytical solutions (Falta, 1995; Rossabi and Falta, 2002; Shan et al., 1992) and numerical simulations (Falta et al., 1992a; Falta et al., 1992b; Sleep and Sykes, 1989) have been made over the years to understand gas flow and make better use of the technology. Recently, horizontal wells have been recognized to be a more effective alternative to vertical wells (Cleveland, 1994; Falta, 1995; Hunt and Massmann, 2000; Sawyer and Lieuallen-Dulam, 1998; Zhan and Park,

1. Porous medium permeability: the soil must be sufficiently permeable to

permit the vapor extraction wells to draw soil gas through the

contaminated domains at a reasonable rate;

2002). The main factors that determine the effectiveness of SVE are:

- 2. Soil water content: water saturation must be low enough to allow sufficient gas flow;
- 3 3. Water solubility: high solubility of contaminant in water requires higher
- 4 gas flow rates or longer gas extraction times to extract contaminants from
- 5 the aqueous phase.

- 7 Shan et al. (1992) found that the well screen locations and porous medium anisotropy
- 8 have strong effects on gas flow patterns. In particular, Shan et al. (1992) found that wells
- 9 should be screened near the bottom of the vadose zone to avoid short-circuiting of the gas
- 10 flow by ground surface inflows of ambient air. Furthermore, the effective radius of an
- SVE well in a medium having a permeability with a large anisotropy ratio (k_h/k_v) is much
- larger than that of a well in a medium having an isotropic permeability.

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- 14 For active methods of removing CO₂, we analyzed similar strategies to those used for
- VOCs by SVE. We show simulation results for horizontal wells, vertical wells, as well
- as the combination of both vertical and horizontal wells, a configuration we have not seen
- in the literature for removal of VOCs.

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Methods

- Numerical simulations were performed using T2CA, a special module of the TOUGH2
- simulator (Pruess et al., 1999), which models flow and transport of CO₂-air mixtures.
- T2CA models five components (H₂O, brine, CO₂, gas tracer, and air) along with heat.
- 23 T2CA uses real-gas mixture properties for density and viscosity, and a Henry's law

formulation for CO₂ solubility. Although capable of non-isothermal simulations, all of

2 the results presented here are isothermal at 15 °C.

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4 In order to compare the effectiveness of the various remediation strategies and scenarios,

5 we define a half-life of the CO₂ plume as the time required for one-half of the initial CO₂

6 mass to be removed from the domain as a convenient measure of the CO₂ removal rate.

7 The initial CO₂ distribution in the model vadose zone corresponds to a steady-state

leakage scenario in which CO₂ flowed buoyantly upward through the saturated zone and

vadose zone, and ultimately seeped out at the ground surface, a process discussed in

detail by Oldenburg and Unger (2003). We present simulation results first for a radial

two-dimensional system to examine passive approaches and vapor extraction with a

vertical well. Next, we present results for an equivalent three-dimensional system to

examine the effectiveness of horizontal wells.

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Simulation results

2-D radial simulations

17 The model domain consists of a cylindrical vertical section of unsaturated and saturated

porous media with a radius of 2100 m. The ground surface is at 35 m elevation and the

water table is at 5 m elevation. The bottom boundary is held at constant hydrostatic

pressure, and the top of the system is held at atmospheric pressure. The outer radial

boundary is held at constant pressure corresponding to the initial CO₂-free gravity-

capillary equilibrium. Properties of the system are shown in Table 1. The porous

medium properties correspond to typical poorly sorted and unconsolidated sediments.

We impose a constant infiltration rate of 10 cm yr⁻¹ with a CO₂ mass fraction of 6.86 x 10⁻⁷. Because of the high solubility of CO₂ in water, this downward water flux is capable of transporting CO₂ as a dissolved component downward to the water table. A leakage rate of CO₂ is set at 4.0 x 10⁵ kg yr⁻¹ over a circular area at the water table with radius 100 m, corresponding to a leakage flux of 4.0 x 10⁻⁷ kg m⁻² s⁻¹. Compared to this rate, CO₂ flux brought by infiltration, which is about 950 kg/y, will not be an important factor. After this leaking system has come to steady state, we obtain the initial condition used for the remediation simulations for the base case in this section. This initial condition for the remediation simulations assumes that a leakage event occurred that brought CO₂ to the vadose zone, but that this event was then stopped, for example by an intervention in the reservoir such as reservoir pressure lowering by CO₂ production. The initial CO₂ plume of approximately 9 x 10⁵ kg (900 tonnes) of CO₂ is shown in Figure 2, where the shaded contours represent CO₂ mass fraction in the gas phase, white contours represent aqueous phase saturation, and vectors represent gas velocities. The initial pressure at the water table is about 5.0 kPa higher than that of the atmospheric. This high pressure difference makes the density effect of CO₂ not that obviously in this study.

Table 1. Properties of the model vadose zone system.

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| Property | Values |
|-------------------------------------|------------------------------------|
| Permeability (m ²) | $1.0 \times 10^{-12} \mathrm{m}^2$ |
| Porosity | 0.2 |
| Res. Water Sat. S _{lr} | 0.1 |
| Res. Gas Sat. S _{gr} | 0.01 |
| Van Genuchten (1980) 1/α (Pa) | $1.0 \times 10^4 \text{ Pa}$ |
| Van Genuchten (1980) m | 0.2 |
| Temperature (°C) | 15 |
| Infiltration (cm yr ⁻¹) | 10.0 |

We analyze four remediation scenarios in the 2-D radial system as follows:

- 2 1. Natural attenuation (passive remediation) without barometric pumping;
- 3 2. Natural attenuation (passive remediation) with barometric pumping;
- 4 3. A 30 m length vertical well whose screen is from elevation 5–20 m;
- 5 4. A 30 m length vertical well with an impermeable surface cover of 50 m
- 6 radius.

The daily barometric pressure record used in the barometric pumping scenario corresponds to an actual pressure variation measured in the Central Valley of California for the year 1997 (Zawislanski et al., 1999). The amplitude of this yearly data fluctuates between $-1.2 \sim 1.8$ kPa around the average pressure which is the same as we used for the atmospheric pressure in the scenarios without barometric pumping. The pressure data are applied repeatedly every year during the whole remediation period. Simulation results after 10 years of remediation for the four cases are shown in Figures 3–6 by the shaded contours of CO_2 gas mass fraction and gas velocity vectors. Although in Figure 4 (barometric pumping scenario) the gas vectors point upwards, we do see vectors towards to opposite direction at some other days during the year when the pressure at the surface is high. The half-life time for each scenario is calculated and listed in Table 2. A pumping rate of 5.0×10^{-4} kg s⁻¹ for Scenario 3 and 4 is used.

Table 2: Half-life times for different scenarios

| Scenarios | 1 | 2 | 3 | 4 |
|---------------------|------|------|------|------|
| Half-life time (yr) | 7.12 | 6.46 | 6.04 | 6.18 |

As shown in Table 2, for passive remediation strategies, barometric pumping (Scenario 2) increases the removal rate of CO₂. This is because when pressure at the ground surface is lower than the average pressure during barometric pumping, more CO₂ seeps out of the ground surface than the case without barometric pumping. This portion of CO₂ will be diluted immediately by the air in the atmosphere gridblocks. When the pressure at the ground surface becomes larger than the average atmospheric pressure, mostly air will flow back into the subsurface from the atmosphere gridblocks. We can also see that that pumping from a vertical well (Scenarios 3 and 4) has increased the CO₂ removal rate slightly. The reason for the limited improvement is that the gas production from the well (pumping rate) is low and limited by the high aqueous phase saturations around the well.

In Scenario 4, an impermeable cover is used at the ground surface. The half-life for this case is 6.18 year, which is longer than for Scenario 3. This somewhat surprising result occurs because the cover at the top decreases the gas pressure gradients and thereby decreases the vertical gas flows needed to remove the CO₂ beneath the cover. In short, while the sweep is more horizontal and therefore potentially more effective in removing CO₂ for the case of an impermeable cover, the vertical flow rates are smaller and the half-life of the plume correspondingly longer.

A sensitivity analysis on how vadose zone thickness affects remediation rates is done for the two passive strategies. The results are shown in Figure 7. As expected, when the vadose zone is thicker, it takes longer for the CO₂ to be removed because more of the CO₂ is located farther from the ground surface for thicker vadose zones. However, the results show an exception in the trend for the case where the vadose zone thickness is 5 m for the case without barometric pumping. In this scenario, the half-life for the CO₂ plume is longer than it was for the 10 m and 15 m thick vadose zones. This reversal in the trend occurs because of the difficulty of removing CO₂ from areas with high aqueous phase saturation, for example, near the capillary fringe. When the water table is close to the ground surface as in this 5 m thick vadose zone case, the CO₂ plume is mostly situated near the capillary fringe where water saturation is high and diffusive and advective transport is limited by low gas-phase saturation, and a significant amount of CO₂ is dissolved in the aqueous phase. In the other cases, the CO₂ plume is mostly above the capillary fringe, transport is faster, and a smaller proportion of the plume mass is contained dissolved in groundwater.

In an attempt to increase the CO_2 removal rate for active remediation, we first tried increasing the pumping rate. However, permeability and high water saturation limited the pumping rate. Therefore, we increased the base-case permeability to $1.0 \times 10^{-11} \text{ m}^2$ and raised the well screen to 20 - 30 m. By doing this, a higher pumping rate of $1.0 \times 10^{-10} \text{ m}^2$ kg s⁻¹ could be applied and significantly increased CO_2 removal was found. To prevent short-circuiting discussed by Shan et al. (1992) we also used a second enhanced method in which an impermeable surface cover with a radius of 50 m exists around the well with the same screen scheme. The half-life times for these two cases are listed in Table 3. When the screen is higher, a cover around the well prevents ambient air at the ground surface from flowing directly to the well, short-circuiting past the contaminated zone. The half-life in this case is shortened by using a cover. In summary, a high well screen

and impermeable surface cover together improve vadose zone CO₂ leakage remediation

effectiveness. Nevertheless, for the case of a vertical extraction well only, significant

CO₂ mass remains in the system away from the pumping well even after 10 yrs of

4 pumping.

Table 3. Half-life for the two high screen cases.

| Higher screen without cover | Higher screen with cover |
|-----------------------------|--------------------------|
| 2.16 year | 1.55 year |

3-D Cartesian simulations

The radial simulations presented above point out limitations of vertical wells, e.g. gas velocities are inversely proportional to distance from the well, and suggest the potential effectiveness of horizontal wells which provide more uniform velocity field. In this section, we use a 3-D Cartesian system to simulate remediation scenarios with horizontal wells. To reduce the computational effort, the horizontal domain was reduced to 300 m in both x and y directions since CO_2 concentration in the gas phase is negligible at r=300 m. To make the 3-D simulations comparable with the radial cases, the initial plume for the 3-D system is obtained by mapping the initial conditions of the radial system into a quarter of a 3-D cylindrical domain. A comparison of the initial CO_2 mass is shown in Table 4, and appears reasonably close to one quarter of the mass in the radial system as it should be, with the discrepancy caused by the smaller model domain and the dissolved CO_2 in gridblocks at radius greater than 300 m in the radial system.

Table 4: Initial CO₂ mass in the two systems

| 2-D radial system | 3-D Cartesian system | 3-D Cartesian system x 4 |
|-------------------------------|-------------------------------|-------------------------------|
| $8.99 \times 10^5 \text{ kg}$ | $2.12 \times 10^5 \text{ kg}$ | $8.48 \times 10^5 \text{ kg}$ |

2 Figure 8 shows the conceptual model for the 3-D Cartesian system consisting of a thick

3 vadose zone and vertical and horizontal wells to be used for vapor extraction. The water

4 table is 30 m below the ground surface. Three base-case scenarios are considered:

6 1. Vertical well only, well screen is from 20 m-30 m;

7 2. Horizontal wells only, of length 90 m aligned with the x- and y-axes at an

8 elevation of 20 m above the bottom of the domain;

9 3. Both vertical and horizontal wells (i.e., combination of Scenarios 1 and 2).

A permeability of $1.0 \times 10^{-11} \text{ m}^2$ and a total pumping rate of $1.0 \times 10^{-2} \text{ kg s}^{-1}$ are used for all scenarios, with other properties the same as shown in Table 1. Simulation results (after 10 yrs of remediation) for each scenario are shown in Figures 9–11. Again, shaded contours represent mass fraction of CO_2 in the gas phase. Note that different contour levels are used in different figures. Figure 12 and 13 are cross sections from Figure 11 shown to elucidate regions hidden from view in 3-D.

Among the three scenarios, the most effective remediation strategy is to use both horizontal and vertical wells. To examine how the length of horizontal wells affects the removal rate, we tested an additional scenario (Scenario 4) that uses a longer horizontal well length of 120 m, but the same total pumping rate. The longer half-life (Table 5)

indicates that a longer horizontal well does not necessarily help if the well reaches

2 beyond where most of the plume resides.

Another scenario (Scenario 5) is a special case to examine how permeability anisotropy affects CO_2 removal. An anisotropy ratio $(k_z/k_y, k_y = k_x)$ of 0.1 is used, where we keep the horizontal permeability unchanged while reducing vertical permeability. Both horizontal wells and vertical well are used. As shown in Figure 14, at early times the removal rate is much faster because of enhanced horizontal flow, while later on the removal rate is slower because vertical flow is relatively restricted. This is consistent with the results found by *Shan et al.* (1992). The half-life time for each scenario is listed in Table 5. In summary, the results of the 3-D Cartesian simulations demonstrate the effectiveness of using both vertical and horizontal wells for removing potential CO_2 leakage plumes from the vadose zone.

Table 5: Half-life for different scenarios in 3-D Cartesian system

| Scenarios | 1 | 2 | 3 | 4 | 5 |
|--------------------|-----|-----|-----|------|------|
| Half-life time(yr) | 2.5 | 1.7 | 0.4 | 1.49 | 0.27 |

Conclusions

The overall conclusion of these modeling studies is that standard passive and active vadose zone remediation strategies will be effective for remediating potential CO₂ leakage plumes in the vadose zone. In detail, the simulation results presented here suggest the following conclusions regarding vadose zone CO₂ leakage plume remediation:

| 2 | 1. | Barometric pumping enhances the removal rate of CO ₂ ; | |
|---|-------|---|--|
| 3 | 2. | Passive CO ₂ removal from high-water saturation regions near the | |
| 4 | | water table is limited by low gas saturation and high solubility in | |
| 5 | | groundwater; | |
| 6 | 3. | For vapor extraction using a vertical well, the well screen should not | |
| 7 | | be too close to the water table; | |
| 8 | 4. | A combination of an impermeable cover and vertical well will improve | |
| 9 | | the removal rate of CO ₂ if the well screen is relatively shallow; | |
| 10 | 5. | The combination of horizontal and vertical wells is more effective than | |
| 11 | | having one or the other; | |
| 12 | 6. | Permeability anisotropy $(k_x > k_z)$ results in a faster removal rate at an | |
| 13 | | early stage and slower rate later on. | |
| 14 | 7. | The combined vertical and horizontal well configuration would be | |
| 15 | | effective for VOC contaminants also. | |
| Acknowledge | nen | ts | |
| We thank Chris Doughty and Stefan Finsterle for thorough reviews. This work was supported by a Cooperative Research and Development Agreement (CRADA) between BP Corporation North America, as part of the CO ₂ Capture Project (CCP) of the Joint Industry Program (JIP), and the U.S. Department of Energy (DOE) through the National Energy Technologies Laboratory (NETL). | | | |
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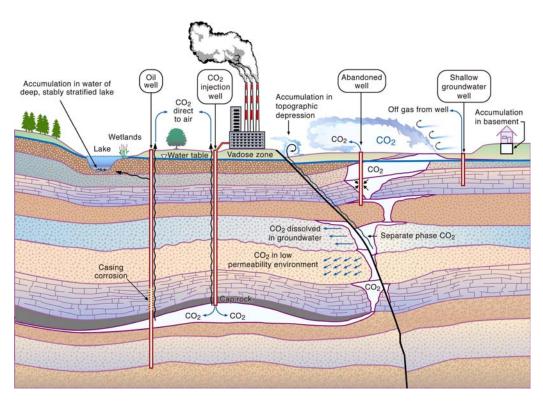


Figure 1. Conceptual diagram of potential leakage and seepage pathways and processes.

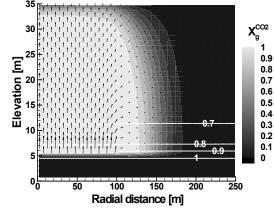


Figure 2. Initial conditions shown by CO_2 gas mass fraction shaded contours, white liquid saturation contours, and gas-velocity. Max. vector represents 8.5 x 10^{-6} m s⁻¹.

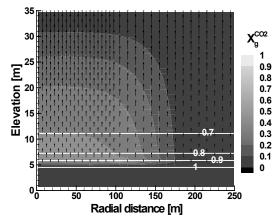
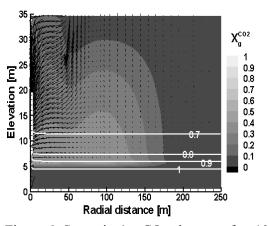


Figure 4: Scenario 2 – CO₂ plume (CO₂ gas mass fraction) after 10 yrs natural attenuation with barometric pumping. Max. vector represents 8.0x10⁻⁷ m s⁻¹.



14 Figure 6: Scenario 4 – CO₂ plume – after 10 15 yrs pumping with a cover. Max. vector 16 represents 4.5 x 10⁻⁴ m s⁻¹.

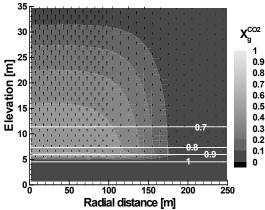


Figure 3: Scenario 1 – CO_2 plume after 10 yrs natural attenuation without barometric pumping. Max. vector represents 4.1 x 10^{-8} m s⁻¹.

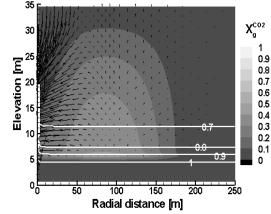


Figure 5: Scenario 3 – CO_2 plume (CO_2 gas mass fraction) after 10 yrs pumping. Max. vector represents 4.5×10^{-4} m s⁻¹.

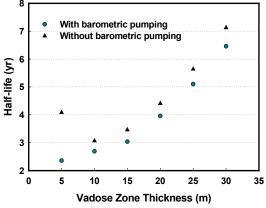


Figure 7: Half-life for different vadose zonethicknesses and scenarios.

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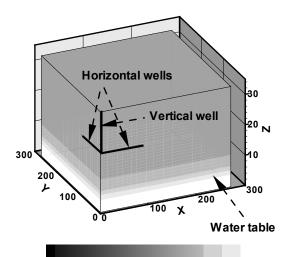
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0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

Figure 8: 3D conceptual model showing horizontal and vertical wells.

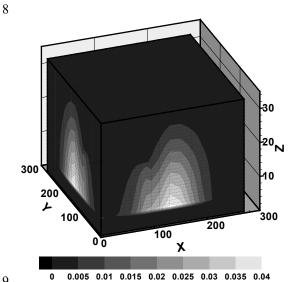


Figure 10: CO₂ plume (CO₂ gas mass fraction) after 10 years of extraction with the horizontal wells.

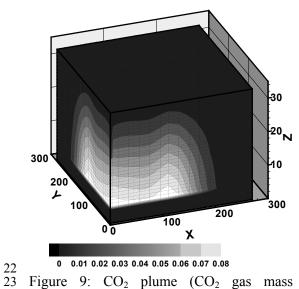


Figure 9: CO_2 plume $(CO_2$ gas mass fraction) after 10 years of extraction with the vertical well only.

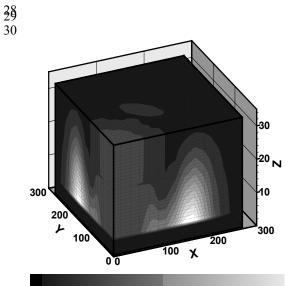


Figure 11: CO₂ plume (CO₂ gas mass fraction) after 10 years of extraction with the both horizontal and vertical wells.

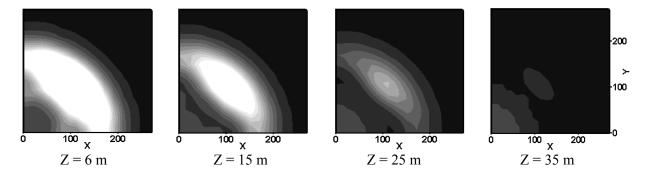


Figure 12: XY-cross section of Figure 11.

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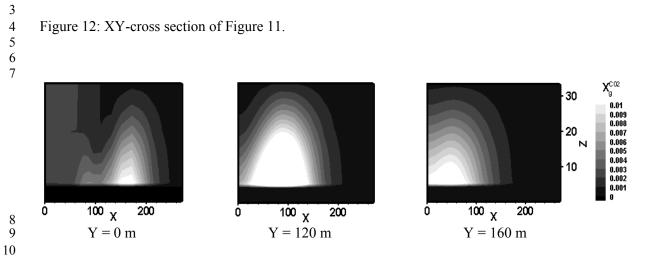


Figure 13: XZ-cross section of Figure 11.

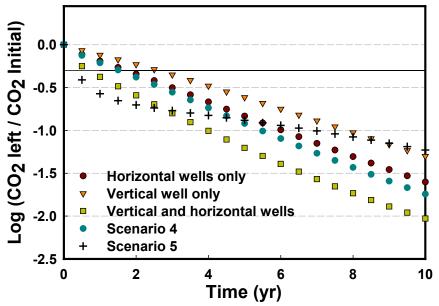


Figure 14: Remaining CO₂ vs. time for different scenarios. The solid horizontal line indicates half-life time.